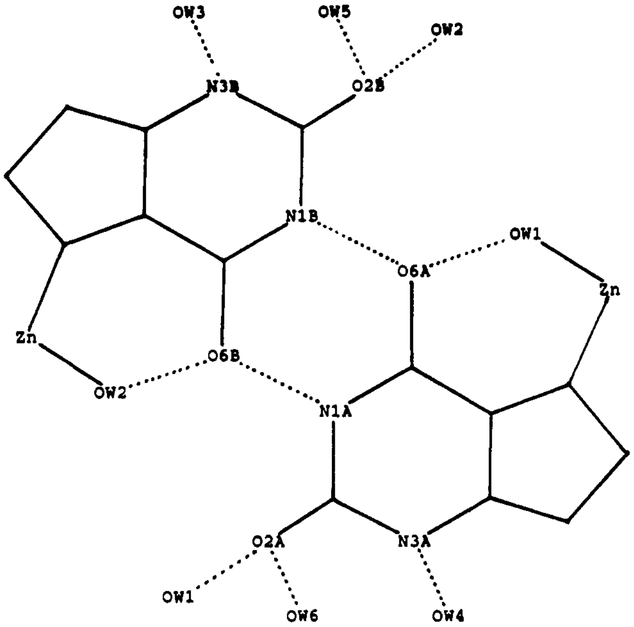
GMP.[42] The pair of interactions N1A → O6B and N1B → O6A, which is very similar to the hydrogen bonds between complementary bases in the two chains that form DNA, are also noteworthy (structure I). Bonds attaching O2 and N3 to water molecules certainly help in the distribution of the negative charge. No purine stacking is to be seen, as is the case with the zinc complexes of the GMP and IMP derivatives.[34]



I

hydrogen bonding in which purine atoms are involved

Ribose A is C2′-exo puckered, whereas ribose B is somewhat irregular, more like C3′-exo; the most usual ribose puckerings are C2′-endo and C3′-endo. Furthermore, the configuration around C4′–C5′ is gauche–gauche for ribose A and trans–gauche for ribose B, the last one being much less frequent than the usual gauche–gauche and gauche–trans.

Finally, we must mention that the values of R and R_w are slightly high. This might be due to the fact that we were unable to locate the hydrogen atoms (about 9% of the electron density) and perhaps to small problems in the refinement process caused by the pseudosymmetry.

Acknowledgment. We are grateful to Michel Simard (Université de Montreal, Montreal, Canada) and Maribel Arriortúa (Universidad del País Vasco, Bilbao, Spain) for their long efforts to solve the structure of MnXao and CuXao, although finally unsuccessful. We also thank Prof. J. Tejada and A. Labarta for the use of their Faraday balance. This research was supported financially by the Spanish Ministry of Education and Science (Grant CICYT 0402/86).

Registry No. MnXao, 133986-23-9; CoIno, 133986-24-0; CoXao, 133986-25-1; NiGuo, 133986-26-2; NiIno, 133986-27-3; NiXao, 133986-30-8; CuXao, 133986-28-4; ZnXao, 133986-29-5; CdXao, 133986-31-9.

Supplementary Material Available: Table S-1 (anisotropic temperature factors), Table S-2 (angles between atoms involved in hydrogen bonding), and Table S-3 (plane calculations) (3 pages); Table S-4 (observed and calculated structure factors) (37 pages). Ordering information is given on any current masthead page.

---

(42) Poojary, M. D.; Monohar, H. *J. Chem. Soc., Chem. Commun.* **1982,** 533.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305,
and Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Electronic Effects of Bis(acetylacetone) in Ruthenium(II) and Ruthenium(III) Complexes

Tai Hasegawa,[†] T. C. Lau,[†] H. Taube,*[,†] and W. P. Schaefer[‡]

Received January 15, 1991

The compound $Ph_4As[Ru(acac)_2Cl_2]$ was prepared by the reaction of $RuCl_3 \cdot 3H_2O$ with acetylacetone in 1 M aqueous KCl. The anion was shown by X-ray crystallography to have a trans configuration, and it is the first *trans*-bis(acetylacetone) complex to have been prepared. The compound crystallizes in the monoclinic system, in the space group $P\bar{1}$, with $a = 10.082$ (2) Å, $b = 13.433$ (2) Å, $c = 14.950$ (2) Å, $\alpha = 65.03$ (1)°, $\beta = 66.71$ (1)°, $\gamma = 72.02$ (2)°, $V = 1663$ (1) Å^3, and $Z = 2$. A number of *trans*-$(acac)_2$ complexes of ruthenium(II), -(III), and -(IV) were prepared from the above compound and were characterized by IR, UV-vis, and ^1H NMR spectroscopy and by cyclic voltammetry. They include *trans*-$[Ru(acac)_2(pyrazine)_2]$ and *trans*-$[Ru(acac)_2(CH_3CN)_2]$. The analogous cis complexes were prepared by the reaction of the ligands pyrazine and CH_3CN with $Ru(acac)_3$ or by thermoisomerization of the trans species, and a comparison of chemical behavior was made. For the acetonitrile derivative, the equilibrium quotient for the isomerization of the trans species to the cis was measured as 80 at 30 °C. Isomerization is so slow for the pyrazine derivative compared to the competing decomposition that a dependable value of the equilibrium quotient could not be determined, but the indications are that the cis form is the more stable. These results, and measurements of the proton affinities of the pyrazine complexes, are rationalized on the basis that when two π-acid ligands compete for π-electron density, this competition is less severe when they are disposed cis, rather than trans, to each other. None of the observations suggest that $acac^-$ acts significantly in a π-acid capacity. When $Ru(acac)_2(CH_3OH)_2$ and pyrazine, mixed in equimolar proportions, react, a very insoluble polymeric material forms. The solid is a poor conductor, but the conductance is increased by a factor as high as 10^6 when it is doped with I_2.

Ligands of the acetylacetone type have played an important role in the development and practice of coordination chemistry.[1] Despite this, little systematic work has been done on the influence it has, acting as a coligand, on the reactivity and properties of a test ligand in a complex. The ligand as the anion is potentially a σ donor, a π donor, and a π acceptor. In undertaking the work to be described, we were particularly interested in the net effect of the three possible modes of interaction and chose for this purpose

---

[†] Stanford University.

[‡] California Institute of Technology.

(1) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: New York, 1978.

0020-1669/91/1330-2921$02.50/0 © 1991 American Chemical Society

Ru(II) as the metal center because of the existing body of work that has been devoted to the same issue with other coligands. Metal centers of the oxidation state 3+ do not provide a useful probe of the π-acceptor capability of acac$^-$ because of the weak tendency of such ions to transfer electron density to π-acceptor ligands. As to metal centers of oxidation state 2+ the following can be stated: the tris complexes are not very useful for present purposes because we are then restricted in composition; with the bis complexes we encounter a pronounced tendency to oligomerize,[2] and in the case of labile centers this greatly limits the range of test ligands which can be introduced. Compared to the octahedral dipositive ions of the first-row transition elements, Ru(II) has two advantages: it has a much higher propensity for back-bonding, and it undergoes substitution much less rapidly. The latter property led us to hope that compositions of the type $Ru(acac)_2L_2$, where L is an easily replaceable ligand such as CH_3OH or H_2O, could be prepared, as worthwhile in its own right and as providing convenient precursors to other compositions. Moreover, because the resulting molecules would be neutral, we expected such species to be soluble in a wide range of nonaqueous solvents, which itself could extend the range of preparative chemistry.

When we undertook our studies, of the mononuclear $(acac)_2$ complexes, only cis forms had been reported, among them *cis*-$Ru(acac)_2(PPh_3)_2$,[3] *cis*-$Ru(acac)_2(CO)_2$,[4] *cis*-$Ru(acac)_2(NO)Cl$,[5] *cis*-$Ru(acac)_2(hia)$[5] (hia is $[(CH_3CO)_2CNO]^-$, the anion of hydoxyiminoacetylacetone), and *cis*-$[Ru(acac)_2(H_2O)Cl]$[6a] and more recently *cis*-β-diketonate complexes of Ru(II).[6b] We set as a special goal the preparation of the trans form, mainly to broaden the scope of the descriptive chemistry and to enable comparisons with cis compounds but in part also to explore the possibility of preparing linear polymers by combining a trans derivative of the type $Ru(acac)_2(H_2O)_2$ with pyrazine in equimolar ratio.

Experimental Section

Materials and Instrumentation. Ruthenium trichloride hydrate, 2,4-pentanedione (Hacac), tetraphenylarsonium chloride hydrate, and pyrazine were obtained from Aldrich and were used as received. Trifluoromethanesulfonic acid was obtained from 3M. All other chemicals were of reagent grade. All organic solvents were of reagent grade and were further purified by standard methods.[7] All syntheses and handling of ruthenium(II) complexes and pyrazine-bridged polymers were done under argon by using Schlenk techniques or in an inert-atmospheric glovebox.

Electronic spectra were recorded on either a Beckman Acta VII spectrophotometer or a Hewlett-Packard Model 8452A diode-array spectrophotometer. Infrared spectra were obtained by using a Perkin-Elmer 577 infrared spectrophotometer or an IBM 98 FTIR spectrophotometer. NMR spectra were obtained by using a Varian 400- or 200-MHz spectrometer. Electrochemical measurements were made with a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system under Ar. With acetone or water as solvent, measurements were performed with glassy carbon, platinum, and saturated calomel as working, counter, and reference electrodes, respectively. Measured values were uncorrected for junction potentials and were calibrated with the hexaammineruthenium(III/II) couple ($E° = 0.05$ V vs NHE) or converted to the NHE scale by adding 0.24 V to the observed potential. With acetonitrile as solvent, measurements were made in a cell outfitted with a Pt^0 working electrode, a Pt^0 auxiliary electrode, and a reference consisting of a Au^0 button electrode immersed in a 1,2-dimethoxyethane solution containing 0.5 M NaO_3SCF_3, separated from the main cell by a Vycor frit. The reference was calibrated with the ferrocene/ferrocenium couple ($E° = 0.55$ V vs NHE) kept in situ. Microanalyses were performed by the Stanford Microanalytical Laboratory or the Analytical Laboratory of the University of California, Berkeley, CA. Conductivity measurements were made on compressed pellets of the complexes, using a four-probe technique.[8]

Preparation of Compounds. $CsCF_3SO_3$. This salt was prepared by dissolving CsCl in neat CF_3SO_3H and then inducing precipitation by adding ether.

***trans*-$Ph_4As[Ru(acac)_2Cl_2]$.** A mixture containing $RuCl_3 \cdot 3H_2O$ (2 g), 10 mL of acetylacetone, and 10 mL of aqueous 1 M KCl was refluxed for 25 min and then was rotoevaporated to dryness. The residue was redissolved in ca. 50 mL of H_2O, and the solution was filtered. Addition of $Ph_4AsCl \cdot xH_2O$ (2 g in 10 mL of H_2O) produced an orange precipitate, which was collected, washed with a little water, and dried in vacuo at ca. 80 °C. The solid was dissolved in $CHCl_3$, and the solution was passed through a short column of neutral alumina. When the column was eluted with $CHCl_3$ and the eluate was rotoevaporated to dryness, an orange crystalline solid was produced, which was further recrystallized from methanol/acetone. Alternatively, a silica gel (Kieselgel 60 silaniert, EM) column was used with H_2O/methanol as eluant. Yields were generally around 20%. Anal. Calcd for $RuAsC_{34}H_{34}Cl_2$: C, 54.19; H, 4.55; Cl, 9.41; Ru, 13.41; As, 9.9. Found: C, 54.04; H, 4.53; Cl, 9.31; Ru, 13.55; As, 10.07.

Also recovered from the eluate, but in small amount, was $Ru(acac)_3$. The major product of the reaction is $Ph_4As[RuCl(acac)(\mu\text{-}Cl)_3RuCl(acac)] \cdot 1.5H_2O$ (vide infra). The binuclear formulation is suggested by the fact that a sharp ^1H NMR spectrum is obtained despite the fact that the oxidation state of Ru is 3+. It is supported by the results of a structure determination by X-ray diffraction,[9] which, though incomplete, was carried far enough to confirm the binuclear structure.

***trans*-$Cs[Ru(acac)_2Cl_2]$.** A saturated solution of $CsCF_3SO_3$ in 5 mL of MeOH was added to *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (55 mg) in 5 mL of MeOH. The resulting red crystalline precipitate was filtered out and washed with a little MeOH and then ether. Yield: 22 mg (60%). Anal. Calcd for $RuCsC_{10}H_{14}Cl_2O_4$: C, 23.87; H, 2.81; Cl, 14.09. Found: C, 23.54; H, 2.70; Cl, 12.22.

***trans*-$Ru(acac)_2Cl_2$.** *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (200 mg, 0.27 mmol) was dissolved in 15 mL of CH_3CN; solid $(NH_4)_2Ce(NO_3)_6$ (144 mg, 0.27 mmol) was added, and after the mixture was stirred for 5 min, a dark green microcrystalline product resulted. This was filtered out, washed with a little CH_3CN, followed by ether, and then recrystallized from CH_2Cl_2/hexane. Yield: 85 mg (85%). The compound was found to be quite sensitive to moisture. Anal. Calcd for $RuC_{10}H_{14}O_4Cl_2$: C, 32.45; H, 3.81; Cl, 19.15. Found: C, 32.47; H, 3.92; Cl, 19.24.

$Ru(acac)_2(CH_3OH)_2$. *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (260 mg) was dissolved in 5 mL of CH_3OH. A few pieces of mossy zinc amalgam were added, and the mixture was stirred gently under argon for 4 h. The zinc amalgam was then removed with tweezers, and the dark brown solid was collected on a frit and washed with a little CH_3OH and then ether. Yield: 6.5 mg (52%). Anal. Calcd for $RuC_{12}H_{22}O_6$: C, 39.67; H, 6.10. Found: C, 39.63; H, 6.25.

***trans*-$Ru(acac)_2(pyz)_2$.** *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (140 mg, 0.19 mmol) and excess pyrazine (300 mg, 3.7 mmol) were dissolved in 10 mL of CH_3OH. A few pieces of zinc amalgam were added, and the mixture was refluxed for 1 h under argon. After cooling, the zinc amalgam was removed and the purplish crystals were filtered off and washed with a little CH_3OH and then ether. Yield: 70 mg (80%). The complex can be recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $RuC_{18}H_{22}N_4O_4$: C, 47.05; H, 4.83; N, 12.19. Found: C, 46.31; H, 4.88; N, 12.04. ^1H NMR (CD_2Cl_2): 1.85 (12 H, s, CH_3); 5.05 (2 H, s, γ-H); 8.25, 8.50 (4 H, d, pyz H).

***cis*-$Ru(acac)_2(pyz)_2$.** $Ru(acac)_3$ (400 mg) was dissolved in a mixture of ethanol (120 mL) and water (20 mL) under Ar. Granular zinc amalgam (10 g) was added, and the mixture was refluxed for 1.5 h. The mixture was filtered while hot and rotary evaporated to dryness. The resulting solid was dried for another 2 h under vacuum to remove unreacted pyrazine and then was recrystallized from methanol. Yield after recrystallization: 40%. ^1H NMR ($CDCl_3$): 1.97 (6 H, s, acac CH_3); 1.99 (6 H, s, acac CH_3); 5.27 (2 H, s, γ-H); 8.10 (4 H, d, pyz H, $J =$ 3.1 Hz); 8.23 (4 H, d, pyz H). ^1H NMR (CD_3OD): 1.94 (6 H, s); 2.01

---

(2) Bullin, J. C.; Mason, R.; Pauling, P. *Inorg. Chem.* **1965**, *4*, 456.

(3) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 1749.

(4) Calderazzo, F.; Floriani, C.; Henzi, R.; L'Eplatteneir, F. *J. Chem. Soc. A* **1969**, 1378.

(5) Mukaida, M.; Nomura, T.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1443.

(6) (a) Mukaida, M.; Yoneda, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3053. Mukaida, M. Unpublished work. (b) Kobayashi, T.; Nishina, Y.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1988**, 1137.

(7) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.

(8) Pierret, R. F. *Modular Series on Solid State Devices*; Addison-Wesley: Reading, MA, 1983; Vol. I.

(9) Red crystals, triclinic, $a = 11.135$ (2) Å, $b = 16.929$ (2) Å, $c = 27.369$ (5) Å, $\alpha = 102.64$ (1)°, $\beta = 100.55$ (1)°, $\gamma = 92.69$ (1)°. Weak layer lines indicate that a is actually 22.270 Å, but the spots are diffuse and those data were not collected. Working in the smaller cell, in space group $P\bar{1}$, we find dimers of formula $Ru_2Cl_5(acac)_2^-$ at three sites, one half-occupied. The arsenic atoms of the tetraphenylarsonium cations were located, but the carbon atoms were not, and thus the structure could not be refined. Final R index = 0.16, with many parameters derived from difference maps. The geometries of the anions in all three sites agree reasonably well; this is our evidence for the formulation given here.

Table I. Crystallographic Data for *trans*-$Ph_4As[Ru(acac)_2Cl_2]$

$RuAsCl_2O_4C_{34}H_{34}$	fw 753.55
$a = 10.082\ (2)$ Å	$P\bar{1}$ (No. 2)
$b = 13.433\ (2)$ Å	$T = 23$ °C
$c = 14.950\ (2)$ Å	$\lambda = 0.71073$ Å
$\alpha = 65.03\ (1)°$	$\mu = 17.06$ cm^{-1}
$\beta = 66.71\ (1)°$	$R_w(F_o^2) = 0.0061$
$\gamma = 72.02\ (2)°$	$R(F_o) = 0.0346$
$V = 1663\ (1)$ Å^3	$Z = 2$
$\rho_{obsd} = 1.51$ g cm^{-3}	$\rho_{calcd} = 1.505$ g cm^{-3}
transm coeff = 0.876–0.722	

(6 H, s); 5.35 (2 H, s); 8.15 (4 H, dd, $J = 1.2, 4.0$ Hz); 8.34 (4 H, dd).

***trans*-$Ru(acac)_2(CH_3CN)_2$.** *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (66 mg) was dissolved in a mixture of acetonitrile (10 mL) and methanol (5 mL). To the solution was added 3 g of granular zinc amalgam, and the mixture was stirred for 1.5 h at room temperature. This solution was rotary evaporated at room temperature and concentrated to ca. 2 mL. An orange solid precipitated, which was collected on a frit and washed with ether. Yield: ca. 20 mg (70%). ^1H NMR (acetone-d_6): 1.78 (12 H, s, acac CH_3); 2.43 (6 H, s, acetonitrile CH_3); 5.14 (~2 H, s, γ-H).

***cis*-$Ru(acac)_2(CH_3CN)_2$. Method 1.** *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ (70 mg) was dissolved in a mixture of acetonitrile (10 mL) and methanol (5 mL). A few pieces of zinc amalgam were added, and the mixture was refluxed for 1 h. This solution was filtered and concentrated to ca. 5 mL. A yellow precipitate formed, which was collected on a frit and washed with ether. Yield: ca. 25 mg (90%). Anal. Calcd for $RuC_{14}H_{20}N_2O_4$: C, 44.09; H, 5.29; N, 7.35. Found: C, 44.10; H, 5.25; N, 7.35. ^1H NMR (acetone-d_6): 1.77 (6 H, s, acac CH_3), 1.81 (6 H, s, acac CH_3), 2.58 (6 H, s, acetonitrile CH_3), 5.20 (~2 H, s, γ-H).

Method 2. $Ru(acac)_3$ (300 mg) was dissolved in a mixture of acetonitrile (50 mL) and water (10 mL) under Ar. Several pieces of zinc amalgam were added, and the mixture was refluxed for ca. 20 min until the purple solution became yellow. After an additional 5 min of refluxing, the mixture was cooled and filtered. The yellow filtrate was rotary evaporated to dryness. The solid was recrystallized from methanol. The cis formulation was confirmed by ^1H NMR spectroscopy. Anal. Calcd for $RuC_{14}H_{20}N_2O_4$: C, 44.09; H, 5.29; N, 7.35; Ru, 26.50. Found: C, 43.85; H, 5.17; N, 7.19; Ru, 26.6.

$Ph_4As[RuCl(acac)(\mu\text{-}Cl)_3RuCl(acac)]\cdot 1.5H_2O$. Anal. Calcd for $C_{34}H_{37}O_{5.5}Cl_5Ru_2As$: C, 41.33; H, 3.77. Found: C, 41.33; H, 3.64. ^1H NMR (acetone-d_6): 2.40 (6 H, s, CH_3); 2.46 (6 H, s, CH_3); 5.99 (~2 H, s, γ-H); 7.90 (16 H, m, *o,m*-H); 7.96 (4 H, t, *p*-H).

Pyrazine-Bridged Polymer. A mixture comprising $Ru(acac)_2(CH_3OH)_2$ (645 mg, 1.78 mmol) and pyrazine (142 mg, 1.78 mmol) in 25 mL of ethanol was heated to ca. 95 °C in a sealed tube for 3 days. After cooling, the mixture was filtered, leaving a dark solid, which was washed with ethanol and then ether. The yields of the solid were generally 98% or above. Anal. Calcd for $RuC_{14}H_{18}N_2O_4$ ($Ru(acac)_2pyz$): C, 44.32; H, 4.78; N, 7.38. Found: C, 43.79; H, 4.82; N, 7.75.

Results

Table II. Final Parameters (x, y, z, and $U_{eq}{}^a \times 10^4$) for *trans*-$Ph_4As[Ru(acac)_2Cl_2]$

atom	x	y	z	U_{eq} or B,^{b} Å^2
Ru1	0	0	0	337 (2)
Ru2	5000	5000	5000	358 (2)
As	940 (0.5)	2841 (0.4)	2559 (0.4)	359 (1)
Cl1	−1410 (2)	1075 (1)	−1133 (1)	519 (4)
Cl2	5296 (2)	3684 (1)	6596 (1)	502 (4)
O1	−1644 (3)	324 (3)	1209 (2)	3.2 (1)*
O2	−667 (3)	−1376 (3)	227 (2)	3.1 (1)*
O3	5719 (3)	3721 (3)	4463 (2)	3.3 (1)*
O4	2896 (3)	4781 (3)	5555 (2)	3.3 (1)*
C1	−3629 (6)	18 (5)	2742 (4)	535 (16)
C2	−2548 (5)	−350 (4)	1855 (4)	3.0 (1)*
C3	−2600 (5)	−1330 (4)	1777 (4)	3.3 (1)*
C4	−1752 (4)	−1768 (4)	1005 (4)	2.8 (1)*
C5	−2074 (6)	−2801 (4)	1030 (4)	497 (14)
C6	5732 (6)	2020 (4)	4373 (4)	605 (17)
C7	4922 (5)	3001 (4)	4725 (4)	3.0 (1)*
C8	3452 (5)	3060 (4)	5277 (4)	3.1 (1)*
C9	2524 (5)	3909 (4)	5636 (4)	2.9 (1)*
C10	924 (6)	3844 (5)	6167 (4)	586 (16)
C11	493 (5)	2046 (4)	4013 (4)	2.8 (1)*
C12	1469 (6)	1147 (4)	4410 (4)	4.2 (1)*
C13	1217 (7)	679 (5)	5477 (5)	5.0 (1)*
C14	15 (6)	1118 (5)	6131 (4)	4.6 (1)*
C15	−961 (6)	1981 (5)	5746 (4)	4.7 (1)*
C16	−744 (6)	2466 (4)	4677 (4)	4.0 (1)*
C21	1573 (5)	4147 (4)	2333 (4)	2.7 (1)*
C22	2297 (5)	4083 (4)	2975 (4)	3.3 (1)*
C23	2840 (5)	4995 (4)	2810 (4)	3.6 (1)*
C24	2613 (6)	5969 (4)	2025 (4)	3.7 (1)*
C25	1882 (6)	6046 (4)	1387 (4)	3.9 (1)*
C26	1382 (5)	5127 (4)	1528 (4)	3.5 (1)*
C31	2538 (5)	2017 (4)	1810 (4)	3.0 (1)*
C32	2536 (6)	923 (4)	1971 (4)	4.1 (1)*
C33	3734 (6)	336 (5)	1408 (4)	4.6 (1)*
C34	4892 (6)	850 (5)	702 (4)	4.4 (1)*
C35	4901 (6)	1922 (5)	534 (4)	4.5 (1)*
C36	3726 (6)	2524 (4)	1083 (4)	3.8 (1)*
C41	−726 (5)	3214 (4)	2101 (4)	2.7 (1)*
C42	−875 (5)	2578 (4)	1625 (4)	3.1 (1)*
C43	−2096 (6)	2835 (4)	1326 (4)	3.8 (1)*
C44	−3146 (6)	3744 (4)	1462 (4)	4.0 (1)*
C45	−3011 (6)	4380 (4)	1940 (4)	3.7 (1)*
C46	−1811 (5)	4116 (4)	2264 (4)	3.1 (1)*

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$. ^{b} Asterisk indicates an isotropic displacement parameter, B.

Determination of the Structure of *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ by X-ray Diffraction. Single crystals of *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ were obtained by slow diffusion of ether into a methanol solution of the complex. A satisfactory crystal was cut from a chunk and glued to a glass fiber. An oscillation photograph showed good crystal quality. A full sphere of data (two equivalent data sets) out to 40° in 2θ was collected, and the two sets were merged; 28 reflections were discarded because of diffractometer error in measuring them. The ruthenium atoms were located by MULTAN[9] at two different centers of symmetry in $P\bar{1}$, and the remaining non-hydrogen atoms were found in a Fourier map. The heavier atoms (Ru, As, Cl) and the methyl carbon atoms were given anisotropic displacement parameters; the oxygen and remaining carbon atoms were treated isotropically, as there was no indication that their apparent motion was anisotropic. Full matrix least-squares refinement included a secondary extinction parameter; the hydrogen atoms were included as fixed contributions at calculated positions or (for the four methyl groups) at idealized positions based on a difference map calculated in their plane, with an isotropic thermal parameter 20% greater than that of the carbon atom they are bonded to. The hydrogen atoms were repositioned twice. Further details are given in Table I. The final difference map showed maximum excursions of +0.61 and −0.38 e Å^{-3}; none of the peaks in the map were interpretable as atoms. No absorption correction was made because the data sets agreed so well; the maximum and minimum transmission factors could have been 0.876 and 0.722 but probably were more nearly equal.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.[10] $R = \sum|F_o - |F_c||/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit $= [\sum(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of data and p is the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.0141\langle I\rangle^2$. The secondary extinction parameter[11] refined to 1.06 (7) × 10^{-6}. Final parameters are recorded on Table II.

The compound shows the trans arrangements of the two chloride ligands and two acetylacetonato ligands about the ruthenium atoms. There are two centrosymmetric half-anions (plus one cation) in the asymmetric unit, and the bond distances and angles agree between them well within the estimated standard deviations (Table III). The Ru–acac geometry is in good agreement with other determinations of Ru–acac structures,[12,13] both of which have

---

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. II, pp 71, 149.

(11) Larson, E. C. *Acta Crystallogr.* **1967**, *23*, 664, eq 3.

Table III. Selected Distances and Angles

	Distances (Å)		
Ru1–Cl1	2.355 (2)	O2–C4	1.288 (6)
Ru1–O1	2.013 (3)	O3–C7	1.283 (6)
Ru1–O2	2.010 (3)	O4–O9	1.281 (6)
Ru2–Cl2	2.362 (1)	C1–C2	1.506 (8)
Ru2–O3	2.014 (3)	C2–C3	1.386 (8)
Ru2–O4	2.016 (3)	C3–C4	1.376 (7)
As–C11	1.905 (5)	C4–C5	1.503 (8)
As–C21	1.903 (5)	C6–C7	1.505 (8)
As–C31	1.896 (5)	C7–C8	1.378 (7)
As–C41	1.908 (5)	C8–C9	1.387 (7)
O1–C2	1.288 (6)	C9–C10	1.502 (8)
	Angles (deg)		
O1–Ru1–Cl1	91.5 (1)	C5–C4–O2	114.3 (4)
O2–Ru1–Cl1	89.8 (1)	C5–C4–C3	119.5 (5)
O2–Ru1–O1	93.8 (1)	C6–C7–O3	114.1 (5)
O3–Ru2–Cl2	87.1 (1)	C8–C7–O3	126.2 (5)
O4–Ru2–Cl2	87.8 (1)	C8–C7–C6	119.7 (5)
O4–Ru2–O3	93.2 (1)	C9–C8–C7	127.8 (5)
C2–O1–Ru1	122.8 (3)	C8–C9–O4	126.0 (5)
C4–O2–Ru1	122.7 (3)	C10–C9–O4	114.7 (5)
C7–O3–Ru2	122.4 (3)	C10–C9–C8	119.3 (5)
C9–O4–Ru2	122.6 (3)	C21–As–C11	105.7 (2)
C1–C2–O1	114.1 (5)	C31–As–C11	110.7 (2)
C3–C2–O1	125.7 (5)	C41–As–C11	111.6 (2)
C3–C2–C1	120.2 (5)	C31–As–C21	107.0 (2)
C4–C3–C2	128.2 (5)	C41–As–C21	111.0 (2)
C3–C4–O2	126.3 (5)	C41–As–C31	110.7 (2)

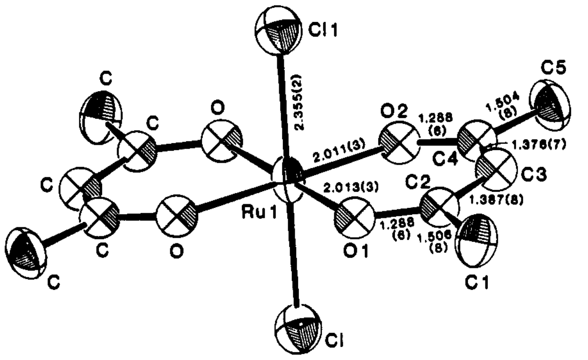


Figure 1. ORTEP drawing of *trans*-$[Ru(acac)_2Cl_2]^-$ with 50% probability ellipsoids. Hydrogen atoms were left out.

cis-acac ligands. The acac ligands and the ruthenium atom are coplanar within 0.1 Å, and the Ru–Cl vector is nearly perpendicular to the plane of the ruthenium atom and oxygen ligand atoms (Table III, Figure 1). There are no short intramolecular contacts.

Further Characterization of the Mononuclear Species. Selected IR peaks of the complexes are shown in Table IV. All complexes show peaks between 1600 and 1500 cm^{-1} characteristic of the acetylacetonate ligand.[14] The 1575-cm^{-1} peak recorded for $Ru(acac)_2(pyz)_2$ is probably due to the centrosymmetric ring stretch of the pyrazine ligand.[15] The dichlororuthenium(III) and -(IV) complexes all show a single Ru–Cl stretch in the far-IR region, which is consistent with the trans configuration (for a cis configuration two peaks would be expected).[14]

The trans configuration for $[Ru(acac)_2Cl_2]^-$ as prepared by following the procedure above is established by the X-ray diffraction data. For all the complexes of the metal in the 2+ oxidation that we describe as trans, ^1H NMR data support this assignment. For the trans configuration, a single methyl resonance is expected and only one is observed. The evidence is strengthened

Table IV. Selected IR Data for Ruthenium Complexes[a]

compd	1600–1500 cm^{-1} [b]	other bonds
trans-Ph_4As-$[Ru(acac)_2Cl_2]$	1546 s, 1522 s, 1513 s	ν(Ru–Cl) 347 m[d]
trans-$Cs[Ru(acac)_2Cl_2]$	1540 s, 1525 s, 1510 s	ν(Ru–Cl) 343 m
trans-$Ru(acac)_2Cl_2$	1520 s	ν(Ru–Cl) 365 m
trans-$Ru(acac)_2(pyz)_2$	1575 s,[c] 1558 m, 1540 m, 1515 s	
cis-$Ru(acac)_2(CH_3CN)_2$	1564 s, 1515 s	ν(CN) 2250 m
$Ru(acac)_2(CH_3OH)_2$	1527 s, 1505 m	

[a] All spectra as KBr pellets. [b] ν(C═O) and ν(C═C) of acetylacetonate ligand. [c] Due to pyrazine ring stretch. [d] There is another peak nearby at 354 cm^{-1}, which is due to Ph_4As^+. This peak is absent in the Cs salt.

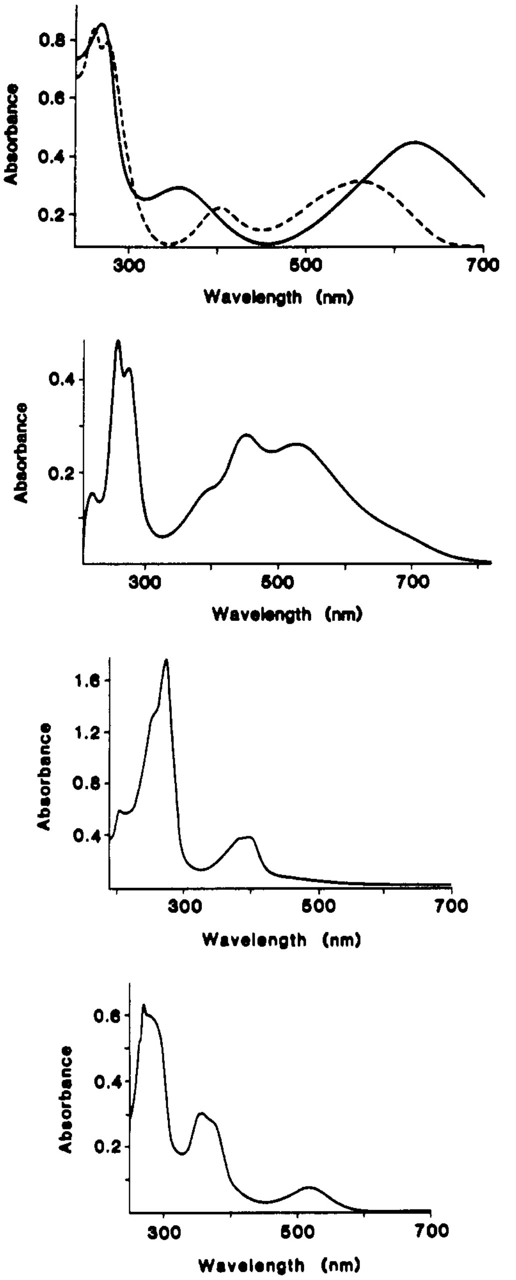


Figure 2. UV–vis spectra of ruthenium bis(acetylacetone) species (top to bottom): (a) *trans*-$Ru(acac)_2(pyz)_2$ (- - -), *trans*-$Ru(acac)_2(pyzH)(pyz)^+$ (—); (b) *cis*-$Ru(acac)_2(pyz)_2$; (c) *trans*-$Ru(acac)_2(CH_3CN)_2$; (d) *trans*-$Ph_4As[Ru(acac)_2Cl_2]$.

---

(12) Bottomley, F.; White, P. S.; Mukaida, M. *Acta Crystallogr.* **1982**, *B38*, 2674.

(13) Chao, G. K.-J.; Sime, R. L.; Sime, R. G. *Acta Crystallogr.* **1973**, *B29*, 2845.

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.

(15) Marchant, J. A.; Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 2160. (CV recorded in 0.1 M Htos and 0.1 M Ktos.)

(16) Lim, H. S.; Barclay, P. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460. (CV recorded in 1 M NaCl(aq).)

Table V. UV-Visible Absorption Data for $Ru(acac)_2$ Complexes

compd	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})	solvent
trans-$Ru(acac)_2(pyz)_2$	567 (14), 401 (9.3), 272 (20), 258 (22)	CH_3OH
trans-$[Ru(acac)_2(pyz)(pyzH)]^+$	620 (5.6), 322 (6.7), 268 (17)	CH_3OH/H_2O (1:4), pH ~ 1.4
cis-$Ru(acac)_2(pyz)_2$	524 (10.4), 452 (11.0), 392 (sh, 6.3), 274 (16.8), 260 (19.1)	CH_3OH
trans-$Ru(acac)_2(CH_3CN)_2$	394 (14), 270 (8.3), 250 (sh, 6.6)	CH_3OH
cis-$Ru(acac)_2(CH_3CN)_2$	397 (6.0), 383 (sh, 5.8), 270 (28)	CH_3OH
trans-$Ph_4As[Ru(acac)_2Cl_2]$	521 (1.5), 376 (5.3), 358 (5.8), 278 (11.3), 272 (12.1), 265 (9.8)	CH_3OH
cis-$Ru(acac)_2Cl(H_2O)$	504 (1.1), 348 (4.9), 282 (9.6)	CH_3OH
trans-$Ru(acac)_2Cl_2$	724 (25.4), 438 (2.4), 338 (4.5), 295 (8.9)	CH_2Cl_2

Table VI. Electrochemical Data (CV)

compd	E_f, V[a]
trans-$Ph_4As[Ru(acac)_2Cl_2]$	0.93, −0.45[b] −0.37[c]
trans-$Ru(acac)_2(pyz)_2$	0.18[d]
cis-$Ru(acac)_2(pyz)_2$	0.26[d]
trans-$Ru(acac)_2(CH_3CN)_2$	0.16[e]
cis-$Ru(acac)_2(CH_3CN)_2$	0.26[e]

[a] All potentials are versus NHE. Scan rate = 100 mV s^{-1}. [b] Measured in 0.1 M KSO_3CF_3 in acetone. [c] Measured in 0.1 M KSO_3CF_3 in water (pH = 4.4). [d] Measured in 0.1 M KPF_6 in acetone. [e] Measured in 1.0 M TBAH in acetonitrile.

by the NMR data for the *cis*-bis(acetonitrile) complex, where two distinct methyl resonances of equal weight are observed. The bis(methanol) complex proved to have a very low solubility in all of the solvents we tried, including water, methanol, ethanol, acetone, dichloromethane, and toluene. Because the compound was prepared under mild conditions, and because the *trans*-bis(pyrazine) compound was prepared from the same precursor in methanol, also at room temperature, we feel confident that the CH_3OH groups occupy trans sites.

The major features of the UV-vis spectra are summarized in Table V. In Figure 2 are shown the profiles for (a) *trans*-$Ru(acac)_2(pyz)_2$ and *trans*-$[Ru(acac)_2(pyzH)(pyz)]^+$, (b) *cis*-$Ru(acac)_2(pyz)_2$, (c) *trans*-$Ru(acac)_2(CH_3CN)_2$, and (d) *trans*-$Ph_4As[Ru(acac)_2Cl_2]$.

A summary of the values of E_f as determined by cyclic voltammetry is shown in Table VI. For $Ph_4As[Ru(acac)_2Cl_2]$ two reversible waves are observed, +0.93 and −0.45 V, which are assigned to the IV/III and the III/II complexes, respectively. The indication from the electrochemical data that Ru(IV) is a readily accessible oxidation state is supported by our preparative work which shows that addition of Ce(IV) to the red Ru(III) complex in CH_3CN produces a dark green species, which chemical analysis indicates as being a Ru(IV) complex. Within the potential range covered by our measurements the bis(pyrazine) and the bis(acetonitrile)ruthenium(II) complexes show a single reversible wave in the CV, which we assign to the III/II couple.

Isomerization. For the bis(acetonitrile) complex, the equilibrium quotient for the isomerization was determined in CD_3OD as solvent, using characteristic ^1H NMR frequencies to determine the ratio [cis]/[trans]. Because of accidental overlap of one of the bands of the CH_3 groups of the cis form with that of the trans, the acetonitrile methyl groups were used. The solutions (3.0×10^{-3} M) were kept shielded from light for the duration of the experiments. At 20 °C, the half-life for approach to equilibrium was found to be ca. 9 days. Small signals appear in the frequency range of coordinated acetonitrile, which are not attributable to either of the bis(acetonitrile) complexes and which we believe are assignable to cis and trans forms of $Ru(acac)_2(CH_3CN)(CH_3OH)$. After 180 days, which is sufficient time for equilibrium to be established, a value for the equilibrium quotient [cis]/[trans] of 80 was determined. One of the frequencies that we attribute to a partly solvated species grew to a maximum but in the final solution was barely detectible, a behavior expected for a species directly related to *trans*-$Ru(acac)_2(CH_3CN)_2$. The other, which we take to be *cis*-$Ru(acac)_2(CH_3CN)(CH_3OH)$, constitutes ca. 0.5% of the total Ru(II) in the final mixture. Free acetylacetone appears, ca. 10% of the total, and also some broadened peaks, indicating decomposition to paramagnetic products. It is unlikely that this very slow side reaction materially affects the determination of the equilibrium quotient we are interested in. In an experiment at 30 °C, where the approach to equilibrium is considerably more rapid ($t_{1/2} \sim 2$ days), values for the equilibrium quotient of 78 and 87 were obtained in approaching equilibrium from both directions (in the experiments described earlier, the trans complex was used). Again there is production of free acetylacetone. At 45 °C, $t_{1/2}$ for approach to equilibrium is ca. 0.25 days, but decomposition is relatively more serious than it is at lower temperatures.

In CD_3CN as solvent, $t_{1/2}$ for isomerization at 20 °C is much greater than 1 month, and even at 70 °C, it is ca. 2 days as compared to $\ll$10 min in CH_3OH as solvent. It was impossible to obtain a value of the equilibrium quotient in acetonitrile because of decomposition that leads to ruthenium products that are NMR silent.

Exchange between CD_3CN as solvent and *trans*-$Ru(acac)_2(CH_3CN)_2$ is much more rapid than is isomerization in the same medium—$t_{1/2}$ at 70 °C $\ll$10 min as compared to 2 days for isomerization. Exchange for the cis form is slower than for the trans: $t_{1/2} \sim 50$ h compared to 10 h (room temperature).

We attempted to determine the rate of isomerization of *trans*-$[Ru(acac)_2Cl_2]^-$ in methanol and found it to be complicated by other reactions. When a solution made up by dissolving the salt in methanol is promptly subjected to TLC, two separate spots of approximately equal intensity of color are formed. We take this to indicate that the dichloro is partially and rapidly converted to the monochloro complex. Both species when collected and reduced by Zn/Hg in CH_3CN are shown by ^1H NMR spectroscopy to retain the trans configuration, nor is any isomerization observed when the solution is kept for 12 h before subjecting it to TLC. In the absence of observations on the cis complex, we cannot distinguish between kinetic and thermodynamic stability of the trans form.

Attempts were made to determine the equilibrium ratio of cis to trans for $Ru(acac)_2(pyz)_2$. We had difficulty finding a deuterated solvent in which the trans compound is sufficiently soluble for NMR measurements to be made. Of them $CDCl_3$ showed the greatest solvent power. We found no hint of the formation of a cis form after keeping a solution of the trans compound in $CDCl_3$ for 7 h at 57 °C. After this time the ^1H NMR signal for coordinated acetylacetone had decreased to roughly half the initial value and it was much broadened.

Experiments were also performed in CD_3OD as solvent. Even after 5 days at 65 °C, no hint of isomerization was observed either for the trans or the cis compounds, but the trans had decreased to 55% of its initial value, while the decrease in the case of the cis was 25%.

The decreases we refer to apparently involve oxidation, a process that becomes more facile when pyrazine (or CH_3CN) is lost from the coordination sphere. Loss of either ligand has a 2-fold effect. The potential of the complex as a reducing agent increases, and moreover, the oxidizing agent (solvent) now has direct access to the metal ion. It is not surprising that oxidation is more rapid in $CDCl_3$ than in CD_3OD. In the former case, the metal can be oxidized by chlorination, and this reaction may well take place as rapidly as pyrazine dissociates; in CD_3OD, presumably D_2 is liberated, but a solvated species such as $Ru(acac)_2(CD_3OD)(pyz)$ may have quite a long life. If in the case of CD_3OD as a solvent there is a simple connection between rate of oxidation and rate of ligand loss, the observations suggest that in this case the cis

Table VII. Conductivity of $[Ru(acac)_2pyz]_n$

sample	conductivity, Ω^{-1} cm^{-1}
(a) undoped polymer	$<10^{-9}$
(b) sample a exposed to air	5×10^{-6}
(c) sample b doped with 5 mol % I_2	5×10^{-4}
(d) sample a doped with 5 mol % I_2	3×10^{-3}
(e) sample a doped with 5 mol % $FeCp_2PF_6$	7×10^{-5}

complex is only slightly more stable than the trans.

Basicity of *trans*-Ru(acac)$_2$(pyz)$_2$. The absorption spectrum of the title molecule was studied as a function of acidity to determine the values of pK_a for the two protic acids that are derivable from it. The measurements were made in solutions 3.0×10^{-3} M in complex, in 75% H_2O/25% CH_3OH by volume. For the determination of pK_a for the first stage of protonation, HCl was used to titrate. The change in spectrum on adding the first proton is shown in Figure 2a, where the absorption maximum is observed to shift from 567 to 620 nm on adding the first proton. Measurements at intermediate acidities yielded as pK_a for the acid dissociation of the monoprotic form the value of 2.6, with agreement at two different wavelengths. The determination of the second pK_a is more difficult because of the low proton affinity of the monoprotonated form. A limiting spectrum is reached in 6 M triflic acid, and from measurements at intermediate values of acid concentration, we conclude that in 1 M HSO_3CF_3, *trans*-$[Ru(acac)_2(pyz)(pyzH)]^+$ and *trans*-$[Ru(acac)_2(pyzH)_2]^{2+}$ are present in equal concentration.

Similar experiments were performed with the cis isomer. In this case, pK_a for the loss of proton from the monoprotic form was found to be 3.0; at ca. 1.3 M HCl, the mono- and diprotic forms are present in equal concentration.

For purposes of comparison, the pK_a corresponding to the deprotonation of *trans*-$[Ru(NH_3)_4(pyz)(pyzH)]^+$ was determined by similar methods. The value found was 0.65.

Pyrazine-Bridged Polymer. On heating of $Ru(acac)_2(CH_3OH)_2$ with 1 mol equiv of pyrazine in EtOH in a sealed tube for several days, a very dark blue solid is produced that is insoluble in all common solvents. A similar solid could also be obtained by reaction of *trans*-$Ph_4As[Ru(acac)_2Cl_2]$ with pyrazine in the presence of zinc amalgam, although in this case care has to be taken to remove all remaining zinc amalgam from the dark blue solid. The polymer can be readily doped with I_2. The purple color of a benzene solution containing a 5–10 mol % equiv of I_2 is rapidly discharged when the polymer is suspended in it. The doped polymer also had a dark blue color and is also insoluble in all common solvents. The polymer can also be doped with $[FeCp_2]PF_6$.

The polymer shows acetylacetonate peaks at 1557, 1538, and 1514 cm^{-1}, indicating that the ligand framework remains unaltered. The centrosymmetric ring stretch of pyrazine that is present at 1575 cm^{-1} as a strong peak in *trans*-$Ru(acac)_2(pyz)_2$ is slightly shifted (to 1577 cm^{-1}) but is greatly diminished in intensity, as is expected if much of the pyrazine on the polymer occupies bridging positions.[17] Hanack et al. reported that the IR spectrum of $FePc(pyz)_2$ (Pc ≡ phthalocyanine) shows a strong pyrazine peak at 1582 cm^{-1} whereas that of the polymeric $[FePc(pyz)]_n$ shows only a very weak shoulder at 1582 cm^{-1}.[18] They estimated the chain length in the polymer to be ≥20. The somewhat relatively higher intensity of the pyrazine stretch in $[Ru(acac)_2pyz]_n$ compared to $[FePc(pyz)]_n$ suggests that the chain length in our material is less than 20.

The IR spectrum of the doped polymer is very similar to that of the undoped one. Mixed-valence pyrazine-bridged oligomers based on *trans*-tetraammineruthenium show characteristic absorption in the near-IR region. In the case of $[Ru(acac)_2pyz]_n$ the spectrum taken from a fluorocarbon mull of the solid between KBr plates shows broad absorption extending from the visible region and tailing all the way to near 3000 nm. The doped polymer gives a similar spectrum with no significant differences from the undoped one.

Conductivity measurements on the polymers are collected in Table VII. The undoped polymer has a very low conductivity of $<10^{-9}$ Ω^{-1} cm^{-1}. Doping with a 5 mol % equiv of I_2 resulted in a conductivity 3×10^{-3} Ω^{-1} cm^{-1}, an increase by over 6 orders of magnitude over the undoped. Simply exposing the undoped polymer to air also resulted in an increase in conductivity, in this case to ca. 5×10^{-6} Ω^{-1} cm^{-1}. Doping the exposed polymer with a 5 mol % equiv of I_2 gave a further increase in conductivity to 5×10^{-4} Ω^{-1} cm^{-1}. Doping with $[FeCp_2PF_6]$ proved to be less effective than with I_2.

Attempts to improve conductivity by heating (for periods of days) $Ru(acac)_2(CH_3OH)_2$ and pyrazine in higher boiling solvents such as propylene carbonate (solution heated at 150 °C) or sulfolane (solution heated at 180 °C) produced solids not significantly different from that made from EtOH heated to only ca. 95 °C.

The mononuclear bis(acetylacetonato)ruthenium(II) complexes we prepared are only sparingly soluble in organic solvents, and undoubtedly the solubility decreases as the molecular weight increases. An important factor limiting the reworking of the polymer is the inertia of the metal centers toward substitution. For labile octahedral metal centers such as Fe(II) and Co(II) or square-planar metal centers, polymers of very long chain lengths can be readily obtained by simply mixing the appropriate reactants together at ambient temperatures.[18] The substitution lability of the bis(acetylacetonato)ruthenium(II) center was investigated cursorily by UV–vis spectrophotometry. Upon heating of a solution of *trans*-$Ru(acac)_2(pyz)_2$ in CH_3CN to 60 °C, the intense peak at 540 nm slowly decreased. A pseudo-first-order rate constant of 10^{-5} s^{-1} was estimated. This represents an upper limit for the rate of replacement of pyz by CH_3CN.

Discussion

In pursuit of the major goal of the research, we hoped to prepare a well-defined bis(acetylacetonate) complex of Ru(II) to serve as a precursor to molecules in which a single π acid competes for electron density derived from the metal. In principle, $Ru(acac)_2(CH_3OH)_2$, which we did prepare, would serve this purpose, but to our surprise, it proved to have only limited solubility in a variety of solvents that we tried as reaction media. Moreover, this species is unstable with respect to the formation of oligomers; if, in the course of the preparation as described, the solution is kept, with stirring, a solid analyzing for one CH_3OH per Ru is obtained. Because of the limited solubility of $Ru(acac)_2(CH_3OH)_2$ and its instability to condensation, we did not find it to be a useful precursor to species such as $Ru(acac)_2(CH_3OH)pyz$ for example, and instead we have resorted to procedures that do not make use of $Ru(acac)_2(CH_3OH)_2$ as an intermediate but that have yielded bis-substituted products. It should be mentioned that efforts were also made to prepare $Ru(acac)_2(H_2O)_2$, but these proved abortive. Moreover, from our experience there is no reason to believe that this species is any more promising for the purposes stated than is the bis(methanol) complex.

Preparations. The conditions for the preparation of *cis*-$Ru(acac)_2(H_2O)Cl$[6a] differ from those which in our work led to *trans*-$[Ru(acac)_2Cl_2]^-$ in the following respects: the Cl$^-$ content was limited to that introduced by the starting material $RuCl_3 \cdot 3H_2O$, ca. 0.16 M Cl$^-$ compared to >1.0 M in our preparation, and the pH was raised to 2.0 by the addition of NaOH (in our case no adjustment of the pH was made). In both cases, the solutions were heated. In the Mukaida preparation, the product solution was evaporated to precipitate a solid, while in our case the anionic product was precipitated from the solution at room temperature. An important difference is the level of Cl$^-$, which in our case was high enough to yield a dichloro product. It is likely

---

(17) Metz, J.; Schneider, O.; Hanack, M. *Spectrochim. Acta* **1982**, *38A*, 1265.

(18) For example: (a) $[M(dmgH)_2bpy]_n$ (M = Fe, Co; $dmgH_2$ = dimethylglyoxime; bpy = 4,4′-bipyridine) was made by warming M(II) sulfate with $dmgH_2$ and bpy in aqueous methanol. Kubel, F.; Strahley, J. *Z. Naturforsch.* **1982**, *367*, 266. (b) $[Fe(acac)_2pyz]_n$ was made by mixing $FeSO_4 \cdot H_2O$ in CH_3OH with H(acac) in pyridine at room temperature. Wei, H. H.; Shya, H. L. *Transition Met. Chem.* **1984**, *9*, 211.

that interconversion between cis and trans forms may be rapid at the temperature of the steam bath so that in both preparations a mixture of cis and trans is present and the outcome in large part is dependent on the separation procedure. The yield obtained in the Mukaida procedure is low, 15%, and it is possible that a trans product may be a large component of the remainder. In our case also the yield is low (20%), but it is known that the binuclear side product comprises the major component of the remainder.

The simple procedure we followed for the preparation of *cis*-$Ru(acac)_2(CH_3CN)_2$, namely reduction of *trans*-$[Ru(acac)_2Cl_2]^-$ at 60 °C in the presence of CH_3CN is a direct application of the results of the equilibrium measurements, which show that, for this composition, the cis form is strongly favored. The behavior of the bis(pyrazine) complex stands in strong contrast: a high yield (80%) of the trans product is obtained from a solution of *trans*-$Ph_4As[Ru(acac)_2Cl_2]$, which is reduced under reflux for 1 h. The experiments on the attempted isomerization throw some light on this behavior, in the sense that once the bis(pyrazine) complex is formed, it is expected to persist.

The qualitative studies on reaction rates for the bis(acetonitrile) complex show that exchange of acetonitrile is more rapid than isomerization. It seems likely that isomerization takes place through a species of reduced coordination number, namely $Ru(acac)_2(CH_3CN)$. The large decrease in rate in CH_3CN compared to CH_3OH as the solvent can then be understood in the following way. If it is assumed that the rate at which CH_3CN is lost from the bis complex is not much different in the two solvents, then the steady-state concentration of the pentacoordinated intermediate will be much greater in methanol than in acetonitrile. This follows because the affinity of $Ru(acac)_2(CH_3CN)$ for CH_3OH is much lower than for CH_3CN. This in turn follows from the very low concentration of $Ru(acac)_2(CH_3CN)(CH_3OH)$ that was observed in the experiments on isomerization in CH_3OH. When the estimate of 0.5% conversion of *cis*-$Ru(acac)_2(CH_3CN)_2$ to the mono(acetonitrile) is used, the equilibrium quotient for the reaction

$$Ru(acac)_2(CH_3CN)_2 + CH_3OH = Ru(acac)_2(CH_3CN)(CH_3OH) + CH_3CN$$

is calculated at 2×10^{-7}. (It is to be noted that the relative molar abundance of CH_3OH and CH_3CN in the equilibrium solution was used in the calculation.) A higher steady-state concentration of the pentacoordinated intermediate, which is the species assumed to undergo rearrangement, means a more rapid rate of reaction.

Electrochemical Data. Of interest is the fact that *trans*-$[Ru(acac)_2Cl_2]^-$, in which Ru is in the 3+ oxidation state, undergoes reversible $1e^-$ oxidation at a potential below 1 V. Back-bonding is not expected to play a role in this range of oxidation states, and the stabilization of Ru(IV) relative to Ru(III) in the environment under present discussion, as compared to that in $Ru(NH_3)_4Cl_2$ where oxidation to the 4+ state is much more difficult, reflects the greater tendency of an anionic ligand compared to NH_3 to release electron density to the metal ion. The comparison of $E_{1/2}$ for the III/II couple, $[Ru(NH_3)_4Cl_2]^{+/0}$ ($E_{1/2} = 0.16$), with that for $[Ru(acac)_2Cl_2]^{-/2-}$ ($E_{1/2} = -0.37$) shows that $acac^-$ stabilizes Ru(III) relative to Ru(II) more than NH_3 does. This is expected on the basis of charge alone, and there is no basis for deciding whether back-bonding is a factor in determining the difference in potential in the two cases.

The cis form of $Ru(acac)_2(CH_3CN)_2$ is found to be somewhat more difficult to oxidize than the trans. Stabilization by back-bonding is expected to be less for the trans species because of a saturation effect: both π acids draw electron density from the same two orbitals, while, in the cis case, all three πd orbitals are used for back-bonding. This competition in the trans case for pyridine is less severe than it is for acetonitrile, but again stabilization is expected to be greater in the cis than in the trans because, in the former case, three πd orbitals are used for back-bonding.

Basicity of Pyrazine as a Ligand. The data that bear most directly on a major goal of this study are those now to be considered. Ideally, in trying to assess the net result of two ($acac^-$) ligands in affecting the electron density at the metal center, it would be desirable to have a single test ligand in the coordination sphere and to have the remaining position occupied by a simple σ donor such as NH_3 or H_2O. But in the absence of a suitable precursor species we have not succeeded in preparing molecules of the desired category and have settled for bis π-acid complexes. Nevertheless, the studies on the proton affinity of pyrazine in *trans*-$Ru(acac)_2(pyz)_2$ as compared to *trans*-$Ru(NH_3)_4(pyz)_2^{2+}$ do shed light on the issue under consideration.

As expected solely on the basis of electrostatics, pyrazine on $Ru(acac)_2$ is found to be considerably more basic (factor ~100) than on $Ru(NH_3)_4^{2+}$. Thus, any contribution by a back-bonding interaction of Ru(II) with $acac^-$ does not overcome the superior tendency of $acac^-$ compared to NH_3 for electron donation. Attention is directed to another feature of the data, namely that the successive dissociation quotients for *trans*-$[Ru(acac)_2(pyzH)_2]^{2+}$ differ by ca. 5×10^2. Considering the large separation between the two basic sites of ca. 9.1 Å, the electrostatic contribution will be small (note that the successive dissociation constants for suberic acid differ by a factor of only 8; the separation of the basic sites in the most extended conformation is close to that in the metal complex). A strong inductive effect is operative in the metal complex, the electron-withdrawing effect of one pyrazine affecting the electron density at the other. Such interactions are much attenuated by the saturated bond system of the organic molecule.

The basicity of the cis isomer, at least in the first stage of protonation where the results are more meaningful, is greater than that of the trans. The finding is compatible with the fact that, in the trans isomer, electron density is withdrawn from only two πd orbitals, while, in the cis form, all three are involved, the electron-withdrawing effect thereby being spread over a larger region.

UV–Visible Absorption Spectra. The simplest spectra to interpret are those of the 2+ species. Most readily accounted for are the absorptions in the visible region at 567 nm for *trans*-$Ru(acac)_2(pyz)_2$ and at 524 and 452 nm for the cis isomer, all of which are ascribable to metal to pyrazine charge transfer. As is also the case for the tetraammine analogues,[19] the trans isomer gives rise to a single band and the cis to two. The bands for the $(acac)_2$ complexes appear at somewhat lower energy than for the tetraammine, in harmony with the evidence adduced in the subsection on basicity, which indicates that a single $acac^-$ is somewhat more electron donating than are two NH_3 molecules. As expected for $\pi^*(pyz) \leftarrow \pi d$ transitions, the absorption moves to lower energy on protonation (see Figure 2). Left to account for in the low-energy region are the bands near 400 nm shown by all of the $(acac)_2Ru^{II}$ species, which we assign to $\pi^*(acac) \leftarrow \pi d$. In the trans complexes, a single band is observed, but in the case of *cis*-$Ru(acac)_2$, where, in contrast to the trans analogue, the absorption in this energy region is clearly resolved, more than one band appears, as expected for the lower symmetry of the cis form. Further in line with this interpretation is the fact that the bands move to higher energy when the pyrazines are protonated, as a result of the stronger electron-withdrawing capacity of pyrazinium ion compared to pyrazine.

The pattern observed for *trans*-$[Ru(acac)_2Cl_2]^-$, $\lambda_{max} = 521$, 376, 358, and 278 nm (excluding the two high-energy peaks ascribable to the accompanying cation Ph_4As^+), is similar to that reported[20] for $Ru(acac)_3$, $\lambda_{max} = 510$, 350, and 270 nm. The lowest energy peak likely corresponds to the process $\pi d \leftarrow \pi(acac^-)$, and if so, the comparison suggests that the two chloride ions are more electron releasing than is one $acac^-$, which seems a quite reasonable outcome considering the difference in charge. If the band at 376 is assigned to $\pi d \leftarrow Cl^-$, the energies of the remaining ones in the two cases are quite similar. We are unable to offer a complete assignment but do suggest that the literature assignment[20] for $Ru(acac)_3$ of the lowest energy transition as $e_g \leftarrow t_{2g}$ is not in keeping with the high extinction coefficient we record for the corresponding transitions in our case.

---

(19) Zwickel, M.; Creutz, C. *Inorg. Chem.* **1971**, *10*, 2395.

(20) Grobelny, R.; Jezowska-Trzebiatowska, B.; Wojciechowski, W. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2715.

Acknowledgment. Support of this work by National Science Foundation Grant CHE-8511658 and National Institutes of Health Grant GM13638-21 (Stanford), National Science Foundation Grant CHE-8219039 for the purchase of the diffractometer, and the Exxon Educational Foundation for other financial support (California Institute of Technology) is gratefully acknowledged, as is the contribution of Dr. Masao Mukaida (Sophia University, Tokyo), in supplying information on the synthesis of *cis*-[Ru(acac)$_2$Cl(H$_2$O)].

Supplementary Material Available: For the Ru–acac complex, Tables SI–SIII and SV, listing assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and full crystal and intensity data (4 pages); Table SIV, listing observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60208-3113

Ligand Tuning Effects upon the Multielectron Reduction and Single-Electron Oxidation of (Bi)pyridyl Complexes of *cis*- and *trans*-Dioxorhenium(V): Redox Thermodynamics, Preliminary Electrochemical Kinetics, and Charge-Transfer Absorption Spectroscopy

M. S. Ram, Lisa M. Jones, Howard J. Ward, Ying-Hsiow Wong, Christopher S. Johnson,
P. Subramanian, and Joseph T. Hupp*

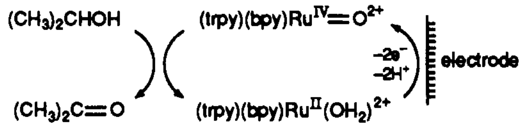
Received October 24, 1990

The effects of ligand substituents upon the electrochemistry and charge-transfer absorption spectroscopy of complexes of the type *trans*-(O)$_2$Re^{V}(py-X)$_4{}^+$ (py-X is a substituted pyridine) and *cis*-(O)$_2$Re^{V}(bpy-Y$_2$)(py-X)$_2{}^+$ (bpy-Y$_2$ is a doubly substituted 2,2′-bipyridine ligand) have been examined. Both series of complexes undergo a simple one-electron oxidation, but the Re(VI/V) potentials (E_f) are roughly 600 mV higher for the trans series compared with the cis. For both series, (bi)pyridyl substituents exert large effects: E_f(VI/V) increases by as much as several hundred millivolts upon replacement of electron-withdrawing substituents by electron-donating groups. Reduction of Re(V) is more complex. For the cis series, and a portion of the trans, it occurs by a two-electron process followed by a one-electron step. For some of the trans species, however, a three-electron reduction (to Re(II)) is seen. Furthermore the reductive reactions are pH dependent, indicating the uptake of protons (and oxo to hydroxo or aqua ligand conversion) upon Re(III) or Re(II) formation. A surprising finding in view of the Re(VI/V) results is that E_f(V/III) is essentially independent of ligand composition for both the trans and cis series. A careful consideration of substituent effects for *cis*-(OH)$_2$Re^{III}(bpy-Y$_2$)(py-X)$_2{}^+$ reduction, which displays both pH-dependent (low and intermediate pH's) and pH-independent (high pH) behavior, suggests an explanation: electron-donating substituents evidently function simultaneously to decrease the affinity of the lower oxidation state for electrons (thereby making E_f more negative) while increasing the affinity for protons (thereby making E_f more positive), resulting in only a small net substituent effect. The electron/proton compensation effect appears also to be operative in the electrochemical kinetics of reduction of *trans*-(O)$_2$Re(py-X)$_4{}^+$. Preliminary experiments show that, at E_f, the two-electron reduction is controlled by the rate of the Re(IV) to Re(III) step and that this step is preceded by a single protonation step. Qualitative rate comparisons, based on cyclic voltammetry peak separation measurements, reveal significant ligand substituent effects. There is no systematic dependence, however, of rate upon ligand electron-withdrawing or -donating character. The lack of correlation is interpreted in terms of compensating "electron demand" and "proton demand" effects in the overall two-electron, two-proton kinetic process. Studies of electronic absorption reveal complex correlations between metal-to-ligand charge transfer (MLCT) energies and E_f(VI/V) for both the cis and the trans series. For the cis series, the charge-transfer absorptions are assigned as Re(V)-to-pyridine (higher energy) and Re(V)-to-bipyridine (lower energy) on the basis of resonance Raman enhancement effects. The effects of solvent on MLCT energies and Re(VI/V) potentials are described in the Appendix. An empirical correlation between both quantities and the so-called solvent acceptor number is found. The correlations are tentatively interpreted in terms of the metal oxidation-state dependence of specific interactions between comparatively electron-rich oxo ligands and electron-deficient solvent functionalities.

Introduction

The growing interest among both inorganic and organic chemists in selective, redox-mediated electrocatalysis has led to a proliferation of mechanistic and synthetic studies of oxo and dioxo transition-metal complexes.[1–5] Oxo-containing species can be quite potent as redox catalysts on account of (1) their ability to stabilize extremely high oxidation states, (2) their ability to

Scheme I



trpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine

---

(1) Representative work: (a) Thompson, M. S.; De Giovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *49*, 4972. (b) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. (c) Dobson, J. C.; Seok, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513. (d) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855. (e) Collin, J. P.; Sauvage, J. P. *Inorg. Chem.* **1986**, *25*, 135. (f) Che, C. M.; Wong, K. Y.; Poon, C. K. *Inorg. Chem.* **1986**, *25*, 1809. (g) Che, C. M.; Ho, C.; Lee, W. O.; Lau, T. C. *Preprints: Symposium on Selective Catalytic Oxidation of Hydrocarbons, ACS Division of Petroleum Chemistry*; American Chemical Society: Washington, DC, 1990; pp 179–186. (h) Yam, V. W. W.; Che, C. M.; Tang, W. T. *J. Chem. Soc., Chem. Commun.* **1988**, 100. (i) Leising, R. A.; Takeuchi, K. J. *Inorg. Chem.* **1987**, *26*, 4391. (j) Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 1472. (k) Charney, L. M.; Finklea, H. O.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 549.

(2) For a review, see: Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221c.

(3) For general reviews of transition-metal oxo chemistry, see: (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

(4) (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. (b) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346. (c) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (d) Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334. (e) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364. (f) Newsham, M. D.; Giannelis, E. P.; Pinnavia, T. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 3885. (g) Brewer, J. C.; Gray, H. B. *Preprints: Symposium on Selective Catalytic Oxidation of Hydrocarbons, ACS Division of Petroleum Chemistry*; American Chemical Society: Washington, DC, 1990; pp 187–191. (h) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

0020-1669/91/1330-2928$02.50/0 © 1991 American Chemical Society